UDC 621.3.032.35:541.182.644

SOL-GEL LUMINOPHORS BASED ON DIOPSIDE

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A relationship is established between the conditions of sol-gel synthesis of powders, their crystallization capacity, and the luminescence properties of crystal phosphors of the composition $CaMgSi_2O_6 : Ti^{4+}$. The properties of materials produced using one-stage and two-stage procedures for heat treatment of the gels are compared. It is shown that the calcination stage has a positive effect on the crystallization process and on the luminescence properties of the articles, and the calcination-stage temperature is a deciding factor in optimization of the heat-treatment procedure.

The class of silicate luminophors is extensive. For many decades they have been produced industrially in many sectors of technology. The main area of application is cathode luminescence, in particular, under hard electronic bombardment [1, 2].

The silicate matrix, which is characterized by high energy of the chemical bonds, provides high thermal, chemical, and radiation resistance in luminophors, while their production cost is relatively low. The possibility of synthesis of silicate luminophors with different luminescence colors (and with high color saturation, if necessary) makes it possible to use them in modern electron-ray sensors with color coding of data [1 – 4].

The quality of light-emitting materials is determined to a large extent by the method of their synthesis. Such methods include sol-gel technology, which allows substantial improvement of the properties of silicate liminophors. The studies described in [5, 6] are devoted to the production of luminescent materials in certain binary silicate systems, using the sol-gel method. Gel-formation parameters and the crystallizing capacity of gels were investigated. These papers noted advantages of the sol-gel method as compared to the traditional technology for synthesis of luminophors.

The purpose of the present study was to establish the relationship between the powder formation conditions, their crystallizing capacity, and the luminescence properties of crystal phosphors of the composition $CaMgSi_2O_6$ activated by titanium ions.

The initial components for homogeneous solutions were tetraethylorthosilicate $Si(OC_2H_5)_4$, calcium and magnesium salts, doubly distilled water, ethyl alcohol, and tetrabutoxyorthotitanate $Ti(OC_4H_9)_4$. The optimum molar content of titanium ions was found earlier by the authors to be equal to

1.2%. The gel formation was carried out at a temperature of 60°C, and the drying of the gels was performed at 100 – 150°C.

Differential thermal analysis was performed on a Q-1500 derivatograph of the Paulik – Paulik – Erday system (Hungary). The crystallizing capacity of the materials was studied on a DRON-3M diffractometer (CuK_α radiation, Ni filter in the range of $2\theta = 12 – 60°$ at a sensitivity of 10^{-3} pulse/sec). Photoluminescence spectra were recorded on a spectrophotometric installation whose main modules are described in [5]. The photomultiplier voltage was 1.6 kV, the spectrum measurement interval was 390 – 660 nm, and the light filter was a UFS-1 ($\lambda = 254$ nm). The cathode-luminescence parameters (the luminosity and the chromaticity coordinates) were determined in a dismountable cathode-ray tube with excitation by an electron beam of energy 2 – 10 keV and current density 0.1 – 10.0 μA/cm². The measurements were carried out in the luminophor laboratory of Platan Company.

The moist gel structure largely determines the structure and properties of the end material. To study the processes occurring in the course of gel heating, differential thermal analysis was carried out (Fig. 1). Four endothermic effects re-
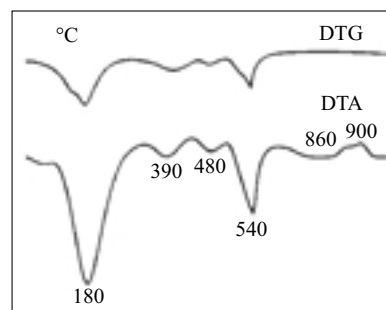

Fig. 1. Data of thermogravimetric analysis of gels.

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lated to weight losses were observed within the temperature interval of $180 - 540°C$. These effects are caused by removal of water and volatile components (about 180°C) and decomposition and melting of magnesium nitrate (about $390 - 480°C$) and calcium nitrate (about 540°C). On further increase in the temperature, the presence of two exothermic effects in the interval of $800 - 900°C$ that are not related to weight losses can be attributed to the process of gel crystallization.

Figure 2 represents the weight loss dependence of a gel in heating. The curve can be arbitrarily divided into three typical segments. In the first segment (up to 200°C), removal of water and organic compounds proceeds at a high rate. Next, a more flattened segment follows (about $200 - 550°C$) that is correlated with the decomposition of salts. In the third segment, the rate and intensity of the process grow once more to some extent. It can be seen that the weight losses in the gels reach a constant level at 600°C. Crystallization does not yet begin at this temperature, and the material remains amorphous.

The crystal structure of luminophors is formed under high-temperature treatment. In the traditional technology for producing the crystal phosphor $CaMgSi_2O_6$: Ti by solid-phase sintering of the mixture components, firing is carried out for 3 h at a temperature of 1250°C [1]. Since one of the advantages of the sold-gel method consists in decreased temperature of synthesis, the heat treatment of the gels was performed in the temperature interval of $1000 - 1200°C$ for 1 h. X-ray phase analysis showed (Fig. 3a) that the main phase in the samples was diopside $CaMgSi_2O_6$ (2.99_x, 2.53_4, 2.89_3, 4.69_1 Å), which is the luminescent phase. In addition, okermanite $Ca_2MgSi_2O_7$ is formed as a secondary phase (2.87_x, 3.09_3, 1.76_3, 5.55_1 Å).

A distinguishing feature of the synthesis of crystal phosphors by the sol-gel method consists in the fact that crystallization begins from an amorphous state. It is known that in producing a fine-crystalline structure (for instance, glass ceramics), it is more expedient to use a two-stage heat-treatment procedure in which crystallization centers are formed in the first stage and growth of crystals occurs in the second stage. With certain assumptions, these recommendations can be used as well for sol-gel synthesis of silicate luminophors.

With the aim of checking this supposition and studying the effect of the heat-treatment procedure on the properties of the materials, the gels were subjected to two-stage heat treatment. Based on the DTA data, the temperature of the first stage (calcination) was varied in the interval of $500 - 800°C$, and high-temperature treatment was conducted at 1200°C. The diffraction patterns of the calcined samples exhibit an amorphous halo, i.e., crystallization processes started at higher temperatures, which agrees well with the DTA data. After these samples are subjected to the high-temperature treatment, the crystal phases appearing, as in the case of the one-stage procedure, are diopside and okermanite (Fig. 3b).

A comparison of the crystallization properties of powders obtained under different heat-treatment conditions
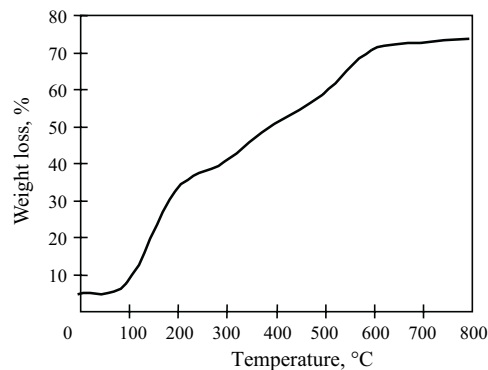

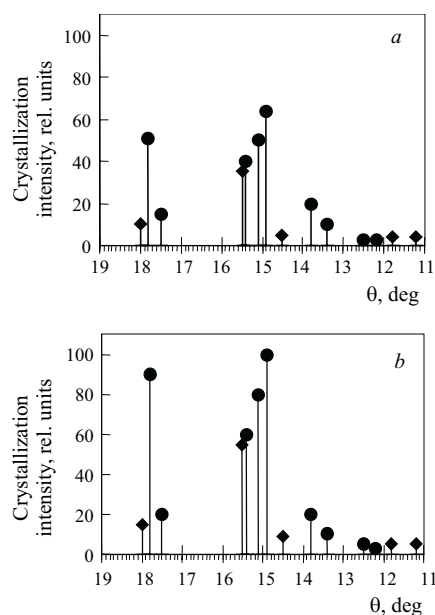**Fig. 2.** Relative weight losses of a gel as a function of the temperature.

Fig. 3. Diffraction patterns of samples produced under various heat-treatment conditions: a) one-stage treatment at 1200°C; b) two-stage treatment at 600/1200°C; ●) diopside; ♦) okermanite.

(Fig. 4) suggests higher intensity of the process in powders that underwent the calcination stage. Furthermore, the largest quantity of the crystal phase is registered in powders with a calcination temperature of 600°C. According to the DTA data, removal of volatile components from the gel structure ends precisely at this temperature, which presumably fosters the maximum rate of crystallization center formation.

It is known that the character of the crystallization has a significant effect on the luminescence properties of powders. All the synthesized materials exhibited photo- and cathode-luminescence properties. Figure 5 shows photoluminescence spectra of some samples. The maximum radiation corresponds to 400 nm, which correlates with the blue spectral range. A comparison of the photo-radiation luminosity of the samples made it possible to conclude that the two-stage
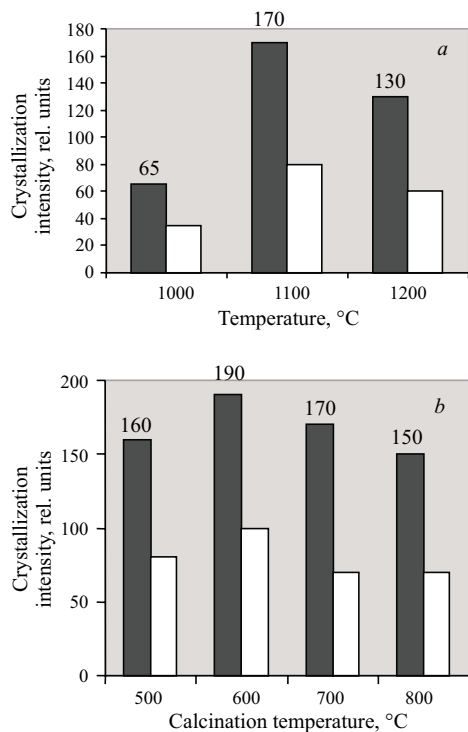
Fig. 4. Intensity of gel crystallization as a function of the calcination temperature: *a*) one-stage heat treatment; *b*) two-stage treatment; ■) diopside; □) okermanite.

Fig. 5. Radiation spectra of luminophors under photo-excitation: *1*) two-stage heat treatment at 600/1200°C; *2*) one-stage heat treatment at 1200°C.

heat-treatment procedure has advantages. And yet, variations in the calcination temperature do not have a perceptible effect on the intensity of the light emission.

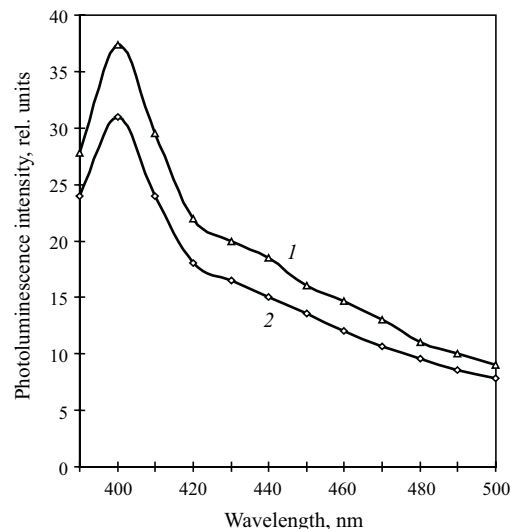Since materials based on $CaMgSi_2O_6 : Ti^{4+}$ are used in electron-ray instruments, the most important service parame-

TABLE 1

Sample	Conditions of synthesis in one-stage heat treatment, °C	Radiation luminance, cd/m^2, under excitation $U \cdot j$, kV · µA/cm^2			Chromaticity coordinates	
		5 · 1	6 · 1	2.2 · 5	X	Y
1	1000	10	12	14	–	–
2	1100	10	16	17	≈ 0.17	≈ 0.17
3	1200	13	17	17	–	–

TABLE 2

Sample	Conditions of synthesis in two-stage heat treatment, °C*	Radiation luminance, cd/m^2, under excitation $U \cdot j$, kV · µA/cm^2				Chromaticity coordinates	
		10 · 1	10 · 2	5 · 1	5 · 2	X	Y
4	500	48	85	17	33	0.123	0.128
5	600	70	132	27	60	0.154	0.124
6	700	55	109	22	44	0.149	0.121
7	800	44	90	18	38	0.142	0.135

* Calcination temperature.

ters of these powders are their cathode-luminescence properties. Cathode excitation has certain features:

– electrons penetrate into a luminophor to a small depth (1 – 5 µm), which increases the role of the surface layers of the powder grains;

– a luminophor nonselectively absorbs cathode-ray energy, and absorption takes place not in luminescence centers, but in the crystal lattice as a whole [1].

Tables 1 and 2 and Fig. 6 show cathode-luminescence properties of materials in relation to the heat-treatment conditions. As in the case of photoluminescence, the maximum luminance under cathode excitation is seen in samples that underwent two stages of heat treatment, namely, calcination at 600°C and annealing at 1200°C. The chromaticity coordinates of such samples also correspond best to the industrial standard K-58 ($X = 0.171$, $Y = 0.147$).

Thus, the two-stage heat treatment is preferable to the one-stage treatment, with respect to both the crystallization processes and the luminescence properties of the material. This is presumably accounted for by the more perfect crystal structure of these luminophors, since crystallization centers arise in the first stage of the heat treatment (calcination) and grow in the second stage. Although the sample remains amorphous after calcination, variation of this temperature within the limits of 500 – 800°C makes it possible to increase the cathode luminance 1.5-fold.

The calcination temperature is a deciding optimization factor, since cathode luminescence is a structure-sensitive property, and all changes in the material structure taking place at the initial stage of the heat treatment are reflected in the cathode-luminescence spectra of the end products. As a result of the research performed, the optimum calcination temperature was found to be 600°C.
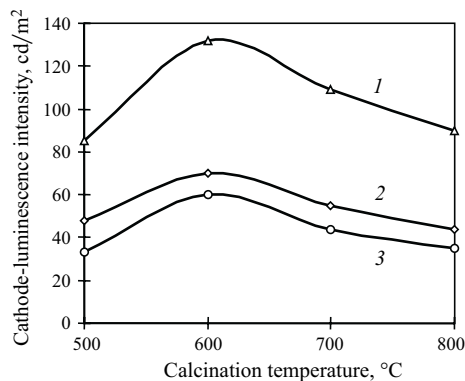
Fig. 6. Effect of the calcination temperature on the cathode-luminescence intensity in excitation $U \cdot j = 10 \times 2$ (*1*), 10×1 (*2*), and 5×2 (*3*) kV $\cdot$ μA/cm^2.

The obtained results confirm one of the main advantages of the sold-gel method, namely, the variety of technological parameters whose optimization at various stages of the synthesis makes it possible to control the properties of the end product.

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